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ENVIRONMENTAL EFFECTS ON SELECTED RESIN
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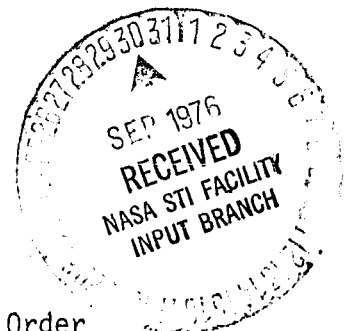
SPACE SHUTTLE ENGINEERING AND OPERATIONS SUPPORT

DESIGN NOTE NO. 1.2-DN-B0104-2

ADVANCED COMPOSITES - ENVIRONMENTAL EFFECTS
ON SELECTED RESIN MATRIX MATERIALS

ENGINEERING SYSTEMS ANALYSIS

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PREFACE

This report is the second of three reports planned to summarize the technology state-of-the-art for graphite and boron reinforced epoxy and polyimide matrix materials. Titles of the reports are as follows:

1.2-DN-B0104-1

"Advanced Composites - Mechanical Properties, and Hardware Programs for Selected Resin Matrix Materials"

1.2-DN-B0104-2

"Advanced Composites - Environmental Effects on Selected Resin Matrix Materials"

1.2-DN-B0104-3

"Advanced Composites - Fabrication Processes for Selected Resin Matrix Materials"

The data and information presented is intended as an adjunct to ongoing NASA studies to determine the relative merits of using composites in the Space Shuttle program.

The other reports document reasons why composites are being considered for more and more aerospace hardware. Designers of high performance aerospace vehicles are constantly seeking ways to save weight and improve performance by employing more efficient structure.

The first report discusses the higher strength allowables that make composites such attractive materials to utilize while the third report deals with the fabrication processes typically employed to make production hardware.

The high strength values reported in the 1.2-DN-B0104-1 document cannot be completely realized for all design applications because

of the potential degrading effect the expected flight environment can have upon composite materials, especially those with a resin matrix. The objective of this report is to identify the effects that expected flight environment can have upon composite properties and the steps being taken by designers and analysts to either alleviate the potential problem or the techniques used to overcome or accommodate them.

SUMMARY

This Design Note documents the effects of environmental phenomena on the mechanical properties of epoxy and polyimide matrix composites. Information was obtained from ten Aerospace Industries' and Government Agencies' reports. Environmental phenomena covered in this report are: water immersion, high temperature aging, humidity, lightning strike, galvanic action, electromagnetic interference, thermal shock, rain and sand erosion, and thermal/vacuum outgassing.

General conclusions arrived at are that resin matrix composites generally are affected to some degree by natural environmental phenomena with polyimide resin matrix materials less affected than epoxies.

INTRODUCTION

This Design Note is intended to furnish design, structures, and materials and processes engineers with information about the effects of various environmental phenomena on selected resin/fiber composites to permit them to evaluate the appropriateness of these materials for Shuttle applications.

Past test programs on composites have indicated that to varying degrees, resin matrix type composites are susceptible to strength degradation with the degree of degradation a function of time exposed to the environment. An understanding of these effects is required if realistic designs are to be obtained. Only when the effects are understood and characterized can logical steps be taken to account for them. For example, current research efforts are aimed at improving well established composite materials. AFML is attempting to alleviate the problem of moisture absorption in epoxy matrix composites by chemical modification or by the use of more hydrolytically stable materials. For chemical modification, the search is for a proper hydrophobic additive. The other approach involves the optimization of the chemistry and processing of matrix polymers.

Various government agencies are also evaluating the long-term environmental resistance of composites. NASA (Langley) for example, will be evaluating graphite/polyimide composites on the YF-12 aircraft during actual service while the material is also being tested in the laboratory after 10,000 hours at 600⁰F. Also, test coupons of various composites are "on-site" at airline terminals to establish long-term, world-wide, environmental data..

Other aerospace organizations and government agencies have also conducted environmental tests, mostly on a laboratory controlled basis. This report will deal directly with data and information obtained from these reports.

DISCUSSION

Information in this section on graphite and boron/epoxy and polyimide matrix composites are based on laboratory controlled environments which are generally more severe than natural phenomena. Results, when used in their proper context, can provide necessary insight to realistically assess a potential design application.

Moisture and Thermal Effects

Test work performed by General Dynamics in Reference 1 shows there are no marked differences in high temperature strength test results between graphite/epoxy specimens exposed to a 24 hour water boil and those exposed to a high humidity/temperature exposure. Data presented in Tables I and II, on two different resin systems, also indicate that maximum cure or postcure temperatures have only a minimal, if real effect on moisture resistance of high temperature epoxy systems.

Experimental data of adhesive-bonded double-lap and scarf joints from Rockwell Report RI-73A01-Vol. 1 (Reference 2) shows that any significant strength degradation was basically in the adhesive system, rather than the boron/epoxy composite itself as a result of moisture environmental exposures.

The variables involved in the double-lap bonded joints were investigated using AF-126-2 and HT 424 adhesives and boron/epoxy to boron/epoxy and boron/epoxy to titanium adherend combinations. The humidity environment of 165°F at 95% RH for 30 days caused some degradation effects with values of 72 and 77 percent of room temperature static strength for the AF-126-2 and HT 424 adhesives, respectively. Single-taper, scarf joint investi-

TABLE I
EFFECTS OF CURE AND POSTCURE ON
UNIDIRECTIONAL HT-S/E-350 LONGITUDINAL
FLEXURE STRENGTH AT 350°F AFTER HUMIDITY EXPOSURE

		FLEXURE STRENGTH				
Cure Temp. F	Postcure Temp. F	Control Ksi	5-Wk 120°F 98% RH Ksi	% Loss	20-Wk 120°F 98% RH Ksi	% Loss
370	375	117.6	161.7	9	141.9	20
370	400	177.6	165.5	7	144.6	19
370	450	181.5	161.5	11	132.5	27
395	375	177.2	165.6	7	146.3	17
395	400	183.0	165.7	9	146.8	20
395	450	180.6	160.7	11	134.2	26
420	400	178.1	163.3	8	153.1	14
420	425	158.2	161.4	+2	155.0	2
420	450	174.1	161.9	7	127.3	27

TABLE II
EFFECTS OF CURE AND POSTCURE ON
UNIDIRECTIONAL HT-S/X-915 LONGITUDINAL
FLEXURE STRENGTH AT 350°F AFTER HUMIDITY EXPOSURE

		FLEXURE STRENGTH				
Cure Temp. °F	Postcure Temp. °F	Control (Ksi)	5-Wk 120°F 98% RH (Ksi)	% Loss	20-Wk 120°F 98% RH (Ksi)	% Loss
370	450	147.2	163.8	+10	115.3	22
395	400	163.9	141.2	14	119.6	27
395	425	157.7	147.8	6	114.1	28
395	450	149.6	127.1	15	131.1	12
420	400	143.1	123.5	14	101.5	29
420	425	135.1	131.3	3	116.6	14
420	450	117.7	134.4	+12	121.0	+3

gations for the temperature/humidity exposure effects at 162°F and 95% RH for 30 days, showed the AF126-2 and HT 424 adhesive bonded joints have a significant degradation in strength. The data averaged 49 and 44% of RT static strength values, respectively.

Adhesive bonded advanced composite test specimens showed that environmental effects are a factor to be considered in selection of the appropriate adhesive system, just as would be the case for conventional metal-to-metal adhesive bonded joints. Correlation between pure resin and composite degradation confirms that water absorption by the resin matrix is the principal factor causing ambient aging problem in reinforced epoxies.

The Rockwell study further showed that boron/epoxy retained a higher percentage of its elevated temperature properties after water boil than graphite/epoxy or glass/epoxy systems. This would support the conclusion that fiber or fiber/resin interface degradation is a contributing factor.

Some work has been done to show that coatings can reduce the effect of moisture absorption. By applying a 0.005 inch flame sprayed aluminum coating to the exposed surface of a boron/epoxy laminate, the weathering degradation for interlaminar shear strength when tested at 300°F was reduced 20% over non-treated specimens. The application of completely impervious coatings such as metal foils to composite parts is not practical. The answer, therefore, is to use a resin/fiber system that (1) shows the least high temperature degradation

after moisture exposure and (2) use suitable reduction factors on the material's design allowables to account for strength reduction due to the environment. Each structural application will have to use a percentage strength reduction based on the expected number of hours and ambient temperature for the vehicle's service life.

Preliminary testing of newer resin systems indicates that Whittaker 5208, Hercules 3501, Fiberite 934 and Ferro E-350 epoxy resins have better elevated temperature strength retentions after moisture exposure than other epoxy matrix composites tested. Evaluation of high-temperature resins by General Dynamics Convair Division (Reference 3) indicates that the polyimides are good candidates for replacement of the epoxies and show minimum effects due to moisture exposure at temperatures up to 600°F.

Boron/epoxy and graphite/epoxy laminates and laminate-faced aluminum honeycomb sandwich specimens have been subjected to thermal pulses specified under military requirements. Thermal pulse testing involves superimposing repeated integrated thermal input cycles onto prestressed advanced composite material, followed by residual strength determination. Thermal pulse cycles from 100°F to 260°F to 100°F and from 100°F to 350°F to 100°F have been used for cyclic thermal conditioning (thermal shock). Exposures of test samples for 500 cycles and 1000 cycles have been undertaken at a rate of one cycle per hour.

Results obtained from specimens exposed to the number of cycles shown above indicate that thermal cycles will cause microcracking of the fiber reinforced composite and also change the moisture absorptivity

coefficient of the material. Therefore, temperature cycling, which can occur in supersonic service, may cause permanent changes in the moisture diffusion behavior of the material. Although all of the absorbed moisture can be removed by drying at 180°F the diffusion behavior is permanently changed. Exposure to sub-zero temperatures, on the other hand, usually does not cause any change in diffusion behavior.

In general, uncoated advanced composites incur a significant strength reduction because of the thermal pulse. Coatings, such as those satisfying lightning strike protection requirements, can also act as thermal protection and minimize or eliminate laminate strength degradation.

The effects of moisture and temperature on material properties are presented in Tables I thru X. The data was obtained from references 1 and 3-8 covering the time period from 1970 thru 1975. Data tabulated in the tables were, in practically all cases, averages of data points recorded from the various test programs reviewed. In some cases reports stated that strengths or moduli presented were calculated averages from "X" number of individual data points. MIL-HDBK-5B, in the section on procedure for calculating design allowables, states that 100 data points may be adequate to allow determination of A and B values, provided the data are near-normally distributed. If the distribution is not normal, at least 300 data points are required so that computation can proceed without knowledge of the distribution form. Since there were not enough data points collected for any one property to allow calculations of MIL-HDBK-5 method design allowables, all property data shown in this note are presented as typical values and should not be used as design allowables.

Table III contains a summary of typical property values for several composite materials after various environmental exposure conditions.

Table IV contains additional data from Reference 1 that further tends to substantiate the small difference in high temperature flexural property values between specimens exposed to a 24 hour water boil and those exposed to a humidity/temperature exposure. Note that the average flexural strength value for control specimens tested at 600°F is lower than for environmentally exposed specimens. Detail review of the data reveals that the control averages based upon six specimens with high-low values being 91.8/78.2 versus only 3 control specimens for the exposed condition with the high-low value 95.2/81.4. The differences again point out the hazard of drawing conclusions based upon tests not conducted with a significant number of replicates.

Additional work conducted by General Dynamics and reported in Reference 7 shows that of two popular graphite/epoxy systems exposed to 24 hours of water boil and flexural strength tested at 350°F, the T300/5208 material retained 15 percent more strength. However, the T300/5208 material lost 18 percent more short beam shear strength. Table V shows the results of this investigation along with comparisons to Kevlar-49/5102 style 101 cloth material.

Matrix dependent properties of a boron/epoxy laminate are seriously affected by both salt spray and humidity exposures but filament dependent properties (0° tensile strength) are negligibly affected by salt spray or humidity exposure. The results of test work conducted by McDonnell Aircraft Company (Reference 4 on Boron/epoxy) are shown in Table VI.

TABLE III
MECHANICAL PROPERTIES AFTER ENVIRONMENTAL EXPOSURE
(TYPICAL VALUES)
(NOT TO BE USED FOR DESIGN ALLOWABLES)

PROPERTY AND EXPOSURE	TEST TEMP. °F	GRAPHITE/EPOXY T300/5708 WHITTAKER	GRAPHITE/EPOXY AS/3002 HERCULES/FIBERITE	EPOXY RESIN X934 FIBERITE	GRAPHITE FABRIC/ 934 EPOXY HMF-3308/34	BORON/POLYIMIDE BORON/5070J WHITTAKER	GRAPHITE/POLYIMIDE MCMOR 11/5070J MONSANTO
FLEX. STRENGTH (KSI) AFTER 24 HRS. H ₂ O BOIL	350	147					
FLEX MODULUS (KSI) AFTER 3 WEEKS 122°F 100% RH	77 250 350			538 296 100			
FLEX STRENGTH (KSI) AFTER 2 HRS. H ₂ O BOIL	350				79.7		
FLEX MODULUS (KSI) AFTER 2 HRS. H ₂ O BOIL	350				8.37		
0° FLEX STRENGTH (KSI) AFTER 500 HRS AT 270°F AFTER 500 HRS AT 350°F AFTER 100 HRS AT 550°F	270 350 550		234 201			138.1	
90° FLEX STRENGTH (KSI) AFTER 500 HRS AT 270°F AFTER 500 HRS AT 350°F AFTER 100 HRS AT 550°F	270 350 550		7.06 7.51 4.9				
SHORTBEAM SHEAR (KSI) AFTER 24 HRS H ₂ O BOIL	350 550	4.64				3.53	
0° TENSILE STRENGTH (KSI) AFTER 100 HRS AT 550°F	550						162
0° TENSILE MODULUS (MSI) AFTER 100 HRS AT 550°F	550						20.7
90° TENSILE STRENGTH (KSI) AFTER 100 HRS AT 550°F	550						4.33
90° TENSILE MODULUS (MSI) AFTER 100 HRS AT 550°F	550						1.2
0° COMP. STRENGTH (KSI) AFTER 100 HRS AT 550°F	550						49.8
0° COMP. MODULUS (MSI) AFTER 100 HRS AT 550°F	550						20.0
90° COMP. STRENGTH (KSI) AFTER 100 HRS AT 550°F	550						9.8
90° COMP. MODULUS (MSI) AFTER 100 HRS AT 550°F	550						0.822
INTERLAMINAR SHEAR STRENGTH (KSI) AFTER 500 HRS AT 270°F AFTER 500 HRS AT 350	270 350		8.8 12.3				

TABLE IV:

ENVIRONMENTAL AGING EFFECTS ON
HM-S/710 GRAPHITE/POLYIMIDE COMPOSITES*

Exposure	Test Temp. (°F)	Flex. Strength (KSI)	Short Beam Shear Strength (KSI)
Controls	75 600	117 85.6	4.23 3.63
24 hrs. H ₂ O Boil	75 600	114 91.0	4.71 3.53
3 wks 120°F 95-100% RH	75 600	104 87.9	4.48 3.26
6 wks 120°F 95-100% RH	75 600	102 86.9	4.18 3.68

TABLE V

ENVIRONMENTAL AGING EFFECTS*
ON EPOXY MATRIX COMPOSITES

Material	Exposure	Test Temp. (°F)	Flex. Strength (KSI)	Short Beam Shear Strength (KSI)
T300/5208	Controls	75 350	248.7 210.9	12.7 7.2
	24 hrs. H ₂ O Boil	75 350	224.8 147.8	11.3 4.6
AS/3501	Controls	75 350	224.3 154.6	17.4 8.5
	24 hrs. H ₂ O Boil	75 350	225.0 128.1	16.1 5.6
Kevlar-49-1/5102 101 Style	Controls	75 350	41.4 25.5	3.60 2.11
	24 hrs. H ₂ O Boil	75 350	33.3 23.4	2.48 1.67

*TYPICAL VALUES NOT TO BE USED AS DESIGN ALLOWABLES

TABLE VI

MECHANICAL STRENGTH OF 0° BORON/EPOXY LAMINATE ^{△3}
AFTER ENVIRONMENTAL EXPOSURE

PROPERTY ^{△1}	TEST TEMP. °F	CONTROL PANEL	5 WEEK ^{△2} HUMIDITY	30 DAY SALT SPRAY
TENSILE STRENGTH (ksi)	R.T.	183	178	160
TENSILE STRENGTH (ksi)	250	156	158	159
TENSILE STRENGTH (ksi)	365	155	107	146

^{△1} Average of 3 specimens.

^{△2} 95-100% RH at 120°F; once a day, except weekends, the panels were removed from humidity and placed in a -65°F chamber for one hour and then in a 250°F oven for one-half hour.

^{△3} SP-296, Composite Materials Corp. Broad Brook, Conn.

Table VII shows that boron/epoxy laminate flexural strength degradation behavior as a function of temperature, is different than for fiberglass/epoxy. Results presented in the table were taken from Reference 4.

Data presented in Table VIII shows that after 100 hours exposure to 550°F both the longitudinal and transverse tensile properties of a graphite/polyimide composite are significantly affected.

ITT in Reference 5 did work to determine the effectiveness of coatings on retention of composite mechanical properties. Protective systems evaluated for boron/epoxy laminates were polyurethane and epoxy paint. Test results shown in Table IX indicate that boron/epoxy panels painted with polyurethane paint degrade slightly less than panels painted with epoxy paint after exposure for three weeks to 100 percent relative humidity. Tests also have shown that polyurethane paint excels over epoxy paint in flexibility, color retention, "chalk" resistance and high temperature capability.

Narmco No. 2387 epoxy resin, the same resin used in 5505 boron/epoxy prepreg, was cast in sheets and exposed to humidity for five weeks. When tested at 365°F the material showed a tensile strength loss of 76 percent. This would indicate that strength losses in epoxy advanced composites is mainly attributed to plasticization of the resin matrix by moisture at high temperature. The data shown in Table X is from the work done by McDonnell Aircraft Company (Reference 4).

TABLE VII

MECHANICAL STRENGTH OF FIBERGLASS/EPOXY AND
BORON/EPOXY COMPOSITES AFTER
ENVIRONMENTAL EXPOSURE

MATERIAL	PROPERTY ①	TEST TEMP. °F	CONTROL PANEL	5 WEEKS HUMIDITY TEST ②	PERCENT DEGRADATION
FIBERGLASS/ EPOXY	FLEX. STRENGTH (ksi)	R.T.	68.2	49.0	28
	FLEX. STRENGTH (ksi)	250	51.0	43.9	14
	FLEX. STRENGTH (ksi)	365	28.1	22.8	19
BORON/ EPOXY	FLEX. STRENGTH (ksi)	R.T.	231	207	10
	FLEX. STRENGTH (ksi)	250	205	174	15
	FLEX. STRENGTH (ksi)	365	164	42	74

① Average of 3 specimens.

② 95-100% RH at 120°F; once a day, except weekends, panels were removed from humidity chamber and placed in a -65°F chamber for 1 hour and then in a 250°F oven for one-half hour.




TABLE VIII

GRAPHITE/POLYIMIDE LONGITUDINAL AND TRANSVERSE
TENSILE PROPERTIES AT 550°F - 100 HR SOAK
MODMOR II/SKYBOND 703

LAMINATE		FAILURE STRESS (PSI)	PERCENT STRESS CHANGE	FAILURE STRAIN (μ in./in.)	PERCENT STRAIN CHANGE	ELASTIC MODULUS (MSI)	PERCENT MODULUS CHANGE
0°	CONTROL	211000		8690		23.2	
	550°F*	162000	-23	7867	-9	20.7	-11
90°	CONTROL	9890		4535		2.03	
	550°F*	4340	-56	4708	+4	1.20	-41

TABLE IX

MECHANICAL STRENGTH OF EPOXY AND POLYURETHANE
PAINTED SP-296 BORON/EPOXY LAMINATE
AFTER THREE WEEK 100 PERCENT RH EXPOSURE

PROPERTY 	TEST TEMP °F	CONTROL PANEL	EPOXY PAINT 	% DEG	POLYURETHANE PAINT 	% DEG
0° Flexural Strength	R.T.	250,000	245,000	2.0	246,000	1.6
0° Flexural Modulus	R.T.	27.9×10^6	27.3×10^6	2.1	28.4×10^6	0
0° Flexural Strength	250	-	227,500	-	221,500	-
0° Flexural Modulus	250	-	25.9×10^6	-	26.2×10^6	-
0° Flexural Strength	350	225,000	92,100	59.1	96,200	57.2
0° Flexural Modulus	350	24.1×10^6	12.8×10^6	46.9	13.4×10^6	44.4
90° Flexural Strength	R.T.	13,200	14,850	0	14,800	0
90° Flexural Strength	250	-	10,500	-	10,500	-
90° Flexural Strength	350	10,200	5,550	45.6	5,750	43.6
Beam Shear	R.T.	14,100	12,900	8.5	13,500	4.3
Beam Shear	250	-	5,950	-	6,430	-



Average of six specimens

TABLE X

MECHANICAL PROPERTIES OF NARMCO NO. 2387 EPOXY TESTED AT 365°F AFTER ENVIRONMENTAL EXPOSURES

PROPERTY 1	CONTROL 2	AFTER 5 WEEK HUMIDITY 3	% DEGRADATION	AFTER 30 DAY 5% SALT SPRAY	% DEGRADATION
JOHNSON SHEAR STRENGTH, PSI	7920	4895	38.2	6245	21.2
TENSILE STRENGTH, PSI	1880	458	75.8	1630	13.3

1 AVERAGE OF 3 SPECIMENS;

2 CONTROL PANELS FABRICATED WITH SAME RAW MATERIAL AND AT SAME TIME AS THE WEATHERED PANELS.

3. PANELS SUBJECTED TO 95-100% RELATIVE HUMIDITY AT $120 \pm 5^\circ\text{F}$; ONCE A DAY, EXCEPT WEEKENDS, THE PANELS WERE REMOVED FROM THE HUMIDITY CHAMBER AND PLACED IN A $-65 \pm 5^\circ\text{F}$ CHAMBER FOR ONE HOUR AND THEN IN A $250 \pm 5^\circ\text{F}$ OVEN FOR 30 MINUTES.

Lightning Strike, P-Static and Electromagnetic Interference (EMI)

Boron and graphite filament organic matrix composite are susceptible to lightning damage, do not dissipate precipitation (P)-static electrical charges, nor provide electromagnetic shielding. Exposure of an unprotected boron or graphite laminate to direct lightning strike can result in severe laminate damage, such as burning or rupture. If an unprotected advanced composite laminate is bonded to an aluminum honeycomb core, the lightning strike can result in dielectric puncture of the laminate, vaporization of core material, and severe disbonding.

Coulomb transfers of only 50 coulombs in one second can cause ignition of the epoxy on the rear surface of an 18-ply boron/epoxy monolithic panel. However, a 120-mesh aluminum fabric can be used to protect an 18-ply B/E panel but not a 7-ply boron/aluminum honeycomb sandwich panel, for reasons which are not fully understood.

Graphite epoxy is much more conductive than boron/epoxy, and therefore, should be less vulnerable. In certain applications, a graphite composite structure may well be able to sustain even a heavy lightning strike without catastrophic damage. The final factor which will determine whether protection must be added will be the laboratory test of the specific composite configuration that is being considered for the intended application.

Air vehicle protruding tips, leading edges, and trailing edges are the exterior mold line surfaces most likely to be primary lightning strike zones; other airfoil surfaces are secondary strike zones. Both must be conductive to dissipate static electricity to ground or to static dischargers.

Lightning protection systems selected for use in advanced composite applications should generally satisfy the following requirements:

- a. Neither protective system nor its application process should detract from advanced composite material properties.
- b. It should withstand mechanical forces involved in dissipating high electrical (lightning) energy loads and provide sufficient conductive surface to sub-structure continuity for safety-of-flight protection from electrical wave forms, i.e., such as shown in MIL-B-5087.
- c. It should permit dissipation and flow of static electricity to sub-structure ground and/or static dischargers ("pigtailed") and should provide adequate shielding for electromagnetic interference (EMI).
- d. Its conductivity characteristics and electrical grounding joint should not significantly degrade with time or operational environment exposure.
- e. Its protective surface material system should be repairable, considering flight and ground service exposure conditions, and require a minimum of maintenance.

Shielding of sensitive and critical electronic equipment from external electromagnetic interference is of vital importance in many types of aerospace vehicle systems, and is most directly accomplished by surrounding such equipment in an electrically conductive shell. Metallic structure performs this function automatically; however, organic matrix advanced composites cannot meet this requirement unassisted because the filaments are not good enough conductors (nor are they well enough

grounded or inter-connected) to absorb by induction external electromagnetic radiation. Fortunately, the basic protective systems necessary to guard against lightning strike damage consist of external conductive materials of one type or another and, consequently, can if properly designed simultaneously serve as effective external EMI shields.

Lightning strike protection systems described in Tables XI and XII can, in general, satisfy some of the lightning design requirements and probably exceed requirements for P-static. The most successful system utilized to date is 120 mesh aluminum wire screen co-cured as the outermost ply of the laminate. Aluminum wire mesh has demonstrated the ability to withstand lightning discharges of 200 KA and is one of the currently predominant shielding systems in use. The data presented in Table XII was abstracted from Reference 9.

Other protection systems of flame sprayed aluminum and aluminum foil will protect against lightning strike but are more than double the weight of the mesh screen. All these systems are bonded to the external moldline facing during the composite cure. Flame sprayed aluminum is repairable, is not restricted by size or shape and has a low maintenance record. The aluminum foil method is the only one that completely seals in the composite surface and is also replaceable.

Galvanic Corrosion

Although resin matrix composites are considered organic in nature, they still can present a problem in galvanic corrosion. All indications are that graphite reinforced composites are more of a problem than

TABLE XI
LIGHTNING STRIKE PROTECTION SYSTEMS

Protection System	Weight (lb/ft ²)	Installation Method	Advantages	Disadvantages
Aluminum flame spray (6 mils)	0.070-0.080	Cocured	<ol style="list-style-type: none"> 1. Independent of surface shape and size 2. Repairable 3. Low maintenance 4. Partial environmental seal of composite surface 	<ol style="list-style-type: none"> 1. Coating weight and quality is operator-dependent 2. Aluminum flame spray quality cannot be determined prior to part cure 3. Limited long-term service fatigue experience record
Aluminum foil (5 mils)	0.070 0.070 + Adhesive	Cocured Adhesive bonded	<ol style="list-style-type: none"> 1. Environmental seal of composite surface 2. Uniform surface conductivity 3. Surface material completely replaceable 	<ol style="list-style-type: none"> 1. Foil stock width limitations 2. Difficult to install on compound contours 3. Poor repairability characteristics 4. Poor part handle-ability characteristics 5. Heaviest system
Aluminum wire mesh	0.030-0.035	Cocured	<ol style="list-style-type: none"> 1. Minimum shape constraint 2. Lightest-weight system 3. Repairable 4. Low maintenance 5. Lowest cost system (mesh cocured with laminate.) 	<ol style="list-style-type: none"> 1. Mesh stock width limitations 2. Inadequate environmental seal for composite

TABLE XII
SUMMARY OF LIGHTNING STRIKE DAMAGE TEST RESULTS

Panel Description	Protective System	Strike Level		Probe Configuration	Weight		Visible Damage/Notes
		Total Coulombs	Time		Initial	Loss	
B/E 18 Ply	None	60	1.72 sec	Rod	339.8 gms	0.4 gms	Burned several paths in top plies. 1/4 dia. hole 0.07" deep at strike. Rear surface ignition.
"	"	95	1.62	Rod	335.8	0.7	Principal burn path 7/8" x 6" in top plies. Hole at strike point ~ 0.05" deep. Rear surface severely charred and bulged ~ 0.02 in. 1/2" diameter.
"	"	135	1.57	Plate	341.3	1.7	Burned 2" x 5" path in top ply. Rear surface charred 3/8 x 1 1/4" and bulged ~ 0.03".
B/E 7 Ply W/Honeycomb	"	51	1.23	Rod	357.5	0.3	Hole thru top 7 plies. Slight charring of rear surface behind strike.
"	"	99	1.37	Rod	354.5	0.1	3/8" dia. hole thru top 7 plies. Slight charring of rear surface. Current took torturous path thru fiber to electrode.
"	"	145	1.23	Plate	342.1	0.7	1/2" dia. hole thru top 7 plies. Charring on rear surface in 1/2" dia. area.
B/E 18 Ply	120 Mesh A1	46	0.60	Rod	355.0	>0.1	Locally burned mesh exposing few fibers. Arc self extinguished.
"	"	51	0.67	Rod			" " " " " " " "
"	"	100		Plate			" " " " " " " "
"	"	102	1.25	Plate			" " " " " " " "
"	"	118	.71	Plate	356.3	0.7	" " " " " " " "
"	"	70	.42	Plate	355.6	0.4	" " " " " " " "
B/E 7 Ply W/Honeycomb	"	100	1.15	"	387.8	0.1	Burned 3/8" dia. hole thru top 7 plies. Rear surface lightly discolored and bulged ~ .005" behind strike.
"	"	204	1.08	"	392.2	2.1	3/4" diameter hole thru top 7 plies. Rear surface charred 3/4 x 1 1/4" area bulged ~ 0.02".

boron reinforced especially when one considers that most airframe structures are made from aluminum which lies below boron in the electromotive series (eg boron is more anodic than aluminum). Graphite on the other hand is more cathodic and can result in severe galvanic corrosion to the anodic material aluminum. Their separation on the galvanic scale is in the same category as aluminum in contact with silver, gold, and platinum. As with corrosion between two homogeneous metals galvanic corrosion between graphite/epoxy and aluminum structure depends on the amount of moisture which penetrates the joint interface.

When one material causes galvanic corrosion of another, an electric current flows from one material to another. By measuring this galvanic current it is possible to calculate how fast the anodic material is corroding. A corrosion current of one microampere per sq. centimeter of corroding surface area is approximately equivalent to a loss of sectional thickness of 1 mil (0.001, inch) per year for the anodic material. Corrosion rates obtained between various composite constituents and 7075-T6 are presented in Table XIII:

TABLE XIII
GALVANIC CORROSION RATE OF 7075-T6 ALUMINUM
IN CONTACT WITH SEVERAL MATERIALS

CATHODE MATERIAL	PEAK CORROSION RATE IN MILS/YEAR	AVERAGE CORROSION RATE IN MILS/YEAR
Abraded Boron	0.0	0.0
Abraded Graphite	24.8	10.0
Graphite/Matrix	2.5	1.2
Titanium	1.4	0.8

The data in Table XIII taken from work A. Morris has done at McDonnell Aircraft Company (Reference 10) show that aluminum in contact with bare graphite filaments (abraded graphite) will corrode almost 18 times as fast as it would in contact with titanium. On the other hand, when the aluminum test panel is coupled to a graphite/resin matrix, composite, the corrosion rate is only 1.8 times that produced by the titanium/aluminum couple.

The safest method of preventing graphite/epoxy parts from causing galvanic corrosion problems would be to use them in contact with materials which are corrosion resistant or assure separation of the adjoining parts (eg - adhesive film between parts, or fasteners with threads covered with a corrosion preventive. Titanium fasteners are compatible with graphite/epoxy and need no corrosion protection. Inconel fasteners are also compatible with graphite/epoxy.

In making mechanical joints between graphite/epoxy parts either titanium or inconel are suitable from a corrosion standpoint. When joining graphite/epoxy to aluminum, titanium fasteners should be used. The approach of using titanium alloys and/or Inconel fasteners can in most designs impose a weight and/or cost penalty. Aluminum alloys are popular structural materials from a cost, weight and availability standpoint. Therefore, it is important that protective methods be developed that will allow use of aluminum alloys as part of a graphite/epoxy assembly. This would include use of 2XXX and 7XXX series alloys for structural components, the 5XXX series alloys for honeycomb core fabrication and titanium, stainless steel or Inconel for fasteners. At present, we do not have sufficient test data to

make predictions on life expectancy of graphite/epoxy - aluminum alloy composite assemblies. Results do indicate that protection is required and, that better protection methods should be developed.

Rain and Sand Erosion

Erosion of advanced composites resulting from rain, sand and dust presents, in general, the same problem as is encountered with fiberglass laminate structures. Although the advanced composite reinforcement properties (such as fiber diameter, tensile strength, and hardness) differ from fiberglass, the matrix resin properties are essentially the same. The relatively brittle advanced composite surface requires some form of protection when exposed to the contaminated airstream.

Conventional paint finishes and lightning strike protective material systems can generally be selected or designed so as to provide a reasonable level of erosion protection for most advanced composite structures (other than leading edges) such as control surfaces, fixed trailing edges, doors, etc. Greater attention is required to provide erosion protection for leading edge structure when speeds exceed 350 miles per hour.

Elastomers such as neoprene or polyurethane, which have been satisfactory in the protection of fiberglass structures, are also applicable to advanced composites. These materials are subject to temperature limitations of 300°F for long periods of time and only a few minutes at 400°F. A new fluorocarbon coating material has been developed at AFML which offers promise for somewhat higher temperatures. This coating is claimed to be able to endure aerodynamic stresses at 425°F for 100 hours.

Outgassing

Organic based materials, used in thermal/vacuum environment around sensitive optical or thermal control surfaces, cannot be allowed to outgas significant quantities of materials that will deposit on these surfaces and cause malfunction. For current manned space applications, specifications normally state that material in a thermal/vacuum environment shall not outgas a total mass loss of 1.0 percent of the original specimen mass and have a maximum Volatile Condensable Material (VCM) content of 0.1 percent of the original specimen mass. These limits, being arbitrary values, may not be appropriate for all applications. From the data shown in Table XIV it appears that most graphite and boron epoxy matrix composites will have no problem meeting the above requirements which are specified in JSC specification SP-R-0022 "Vacuum Stability Requirements of Polymeric Materials for Spacecraft Applications."

TABLE XIV
OUTGASSING DATA ON TYPICAL COMPOSITE MATERIALS

<u>Material</u>	<u>Panel Fabricator</u>	<u>Testing Agency</u>	<u>Total Weight Loss (%)</u>	<u>VCM (%)</u>
Type I/5208	Lockheed	NASA/Goddard	0.093	0.014
HM-S/BP-907	Hercules, Inc.	Ball Bros.	0.079	none
A-S/3501	Hercules, Inc.	Ball Bros.	0.159	none
HM-S/X-904	Convair	NASA-MSFC	-	none
HT-S/E-350	Convair	NASA-MSFC	-	none
A-S/3501	Rockwell Int.	Sandia Corp.	0.77	none
Modnor II/1004	Rockwell Int.	Sandia Corp.	0.49	0.009
Carbon/Epoxy	Goodyear	NASA-GSFC	0.55	0.01
Rigidite 5505	Whittaker	JPL	0.46	0.01
Boron/828,1031	Shell Chemical	JPL	0.25	0.02
HY-E-1002	Fiberite Co.	JPL	0.32	0.04
HY-E-1001	Fiberite Co.	JPL	0.53	0.04
HM-S/4617	-	NR/NASA	0.63	0.03
HM-S/4617 v/Al coat	-	NR/NASA	0.55	0.02
T300/934	-	Goddard	0.28	0.01
Boron/SP296	Rockwell Int.	NASA/MSFC	0.25	0.01

CONCLUSIONS

Moisture and Thermal Effects

- (1) A high temperature (above 250⁰F) strength loss caused by moisture or humidity exists with all epoxy matrix advanced composite systems. The effects are greater with graphite than with boron.
- (2) Mechanical property losses in advanced composites is mainly attributed to plasticization of the resin matrix by moisture at high temperatures.
- (3) Filament dependent properties of boron/epoxy composites are negligibly (maximum of 12% degradation) affected by either 5% salt spray or 100% relative humidity environments.
- (4) The mechanical strength of fiberglass/epoxy laminates, after five weeks of 120⁰F/95% RH environmental exposure degrades three times more than boron/epoxy exposed to the same environment when tested at room temperature; degrades equally with boron/epoxy (15%) when tested at 250⁰F; and degrades one-fourth as much as boron/epoxy when tested at 365⁰F.
- (5) Weathering degradation of boron/epoxy laminates is reduced to a maximum of 20 percent by applying a 0.005" flame sprayed aluminum coating to the exposed surface.
- (6) Epoxy matrix composites painted with polyurethane paint degrades slightly less than panels painted with epoxy paint after 3 weeks of 100 percent RH environment and noticeably less (up to 20%) than unpainted panels.

- (7) The high temperature strength properties of graphite/polyimide (710) composite system are not affected by moisture.
- (8) Whittaker 5208, Hercules 3501, Fiberite 934 and Ferro E-350 epoxy resin have among the highest elevated temperature strength retentions after moisture exposure of the epoxy resin systems.
- (9) Uncoated graphite/epoxy composites' strength is affected by cyclic thermal conditioning.
- (10) Thermal protective coatings, such as those used for lightning strike protection can help minimize or eliminate laminate strength degradation affects.
- (11) Thermal shock effects on advanced composites sandwich facings having a protective thermal coating are further minimized as a function of the core material heat capacity.

Lightning Strike and Electromagnetic Interference (EMI)

- (12) It is concluded that coulomb transfers of less than 60 coulombs can locally heat the rear surface of an 18-ply B/E panel to its ignition temperature, whereas a 7-ply boron/aluminum honeycomb sandwich can sustain much larger coulomb transfers without igniting. The 120 mesh aluminum fabric does protect the 18-ply panels but do not protect the sandwich panels.
- (13) Organic matrix advanced composites cannot meet the shielding requirements unassisted for sensitive and critical electronic equipment from external electromagnetic interference.
- (14) Basic protective systems necessary to guard against lightning strike damage can simultaneously serve as effective external EMI shields.

Galvanic Corrosion

- (15) Graphite/resin composites can cause severe corrosion of aluminum and most fastener materials. A cautious and conservative approach must be taken in designing a graphite/resin-metallic structure.

Rain and Sand Erosion

- (16) Erosion resistance of resin matrix composites is essentially the same as normal fiberglass laminate.
- (17) Materials such as neoprene or polyurethane elastomer coatings, which are satisfactory for protection of fiberglass laminate structure against rain and sand erosion, can also be effective on advanced composite materials.

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